

## REDUCED COST CLEANUP OF GROUND WATER USING PUMP AND TREAT AND TWO NEW *IN SITU* TECHNOLOGIES

Leland W. Younker  
Lawrence Livermore National Laboratory  
P.O. Box 808, L-203  
Livermore, CA 94551  
(510) 422-6472

Alan B. Copeland  
Lawrence Livermore National Laboratory  
P.O. Box 808, L-627  
Livermore, CA 94551  
(510) 422-8188

### ABSTRACT

A project is being conducted at Lawrence Livermore National Laboratory (LLNL) to demonstrate the application of a combination of technologies designed to reduce the total cost of cleaning up VOCs in ground water to the point of formal closure of remedial activity. Essential elements of this project include: a solid functional understanding of site hydrogeology and contaminant distribution; an effective pump and treat system for boundary plume control and distal plume cleanup; and field experience with critical elements of new *in situ* methods to be used for rapid contaminant source area remediation. The new methods are *in situ* hydrous pyrolysis/oxidation achieved by injecting steam and oxygen into the contaminated source region and *in situ* microbial filters which use a resting-state bioaugmentation technique to remove contaminants at the periphery of the treated source area. The project includes a strategy for developing both appropriate future application sites as well as commercial practitioners of the application of these remediation technologies.

### INTRODUCTION

In order to develop the necessary parameters for a faster and lower total cost ground water plume remediation strategy, a demonstration project has been started at the Lawrence Livermore National Laboratory Livermore Site. The technical approach capitalizes on experience gained in a CERCLA driven restoration project currently underway at that site. Remediation of ground water contaminated with VOCs at LLNL's Livermore Site was initiated in 1989. The Site was placed on the EPA Superfund National Priorities List in 1987, and in 1992 the regulatory agencies and DOE signed a Record of Decision (ROD) governing the cleanup of the site. The approved ROD specifies the arrest of the downgradient offsite movement of the plumes

followed by remediation of the onsite source areas to reduce cleanup time. Contaminant concentrations above Maximum Contaminant Levels (MCLs) occur under about 85% of the Site as shown in Figure 1.

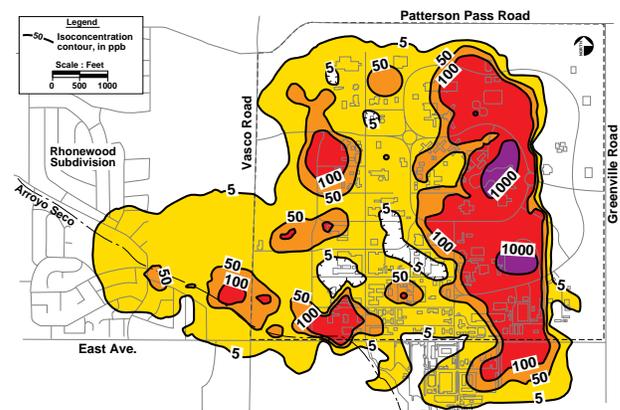


Figure 1. Contours of total VOC concentration superimposed on a map of the LLNL Livermore Site. Southwest and southern portions of the plume are beyond the site boundary.

Through a series of continually advancing pump and treat techniques (Hoffman, 1993), LLNL has demonstrated that rapid cleanup of the distal portions of contaminated ground water plumes (distal as defined in Figure 2) is feasible and by the end of 1996 the first ROD requirement will have been achieved. As evidence of progress, contaminant concentrations at the southwest corner of the site in one hydrostratigraphic unit are given in Figure 3. Substantial reduction of contaminant concentration in the offsite plume is the result of six years of operation in this area. Three dimensional computer model simulations, calibrated to measured data, predict attainment of VOC contamination levels in the distal plume in the low 10's of ppb in 10–15 years (Gelinias, *et al.*, 1996).

Source area remediation is more difficult and requires more aggressive cleanup techniques than for the distal portions of the plumes. Contaminants at the source exist in both the fine-grained and the coarse-grained sediments. Approximately 90% of the contaminant mass at the site is present in the source regions. Because of low hydraulic conductivity of the fine grained-sediments, cleanup time for these sediments using pump and treat is significantly longer than that required to remediate the distal, more permeable zones. In addition, retardation mechanisms in the fine-grained materials have a greater impact than those of the higher permeability sediments. Thus, source region cleanup drives the time required to achieve acceptable restoration, as well as the total cost.

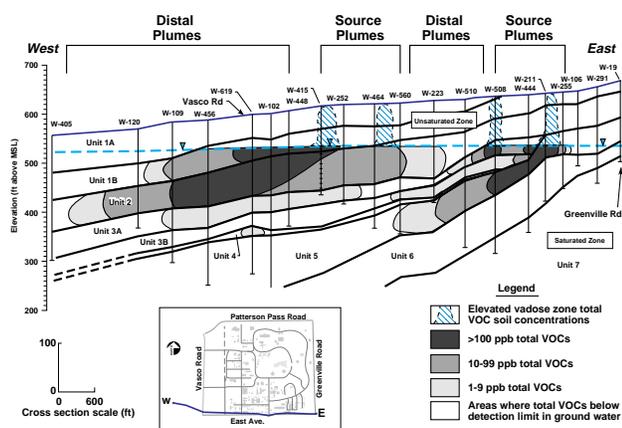


Figure 2. East-West cross-section at southern boundary of the LLNL Livermore Site showing hydrostratigraphic units with VOC contaminant concentrations. Source and distal regions are defined as indicated.

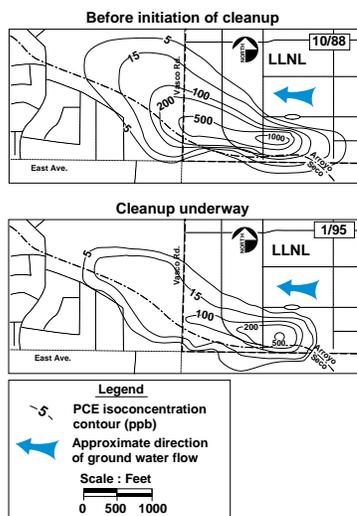


Figure 3. VOC plume contours in 1988 and 1995 in Hydrostratigraphic Unit 1B showing 500 ppb contour pulled back 1,200 feet.

## CLEANUP STRATEGY

Our current approach to achieve lowest cost to closure of the LLNL Livermore Site focuses on using new technology to accelerate mass removal to eliminate contaminant source regions while pump and treat sustains boundary control and finishes distal plume cleanup. As discussed above, pump and treat systems are currently operating successfully at LLNL.

The technical approach to source remediation was chosen using the following criteria to meet LLNL objectives:

- *in situ* (extraction and above ground treatment not required)
- operable at depths averaging 125 ft.
- effective in the saturated zone
- rapid contaminant destruction:
  - for concentrations up to and exceeding saturation
  - to reduce concentrations to MCLs
  - for large volumes
- deployable at a commercially useful scale within 2 to 3 years.

The selected approach, called hydrous pyrolysis/oxidation, is an extension of Dynamic Underground Stripping which we believe can meet the above criteria. The process, described in detail below, operates through the injection of steam and oxygen into the contaminated zone, which results in rapid oxidation of the VOCs.

A method to contain the source region and prevent its expansion is required during the application of hydrous pyrolysis/oxidation. The injection of large volumes of steam will accelerate contaminant migration and be a force for source region dispersal (Figure 4). We have evaluated both extractive and permeable barrier candidate technologies and, in general, the large volumes of ground water required to be treated over a short period of time preclude the deployment of extractive technologies. The following selection criteria have been applied to meet our remediation objectives:

- *in situ* and non-extractive
- operable at depths averaging 125 ft.
- effective in the saturated zone
- rapid contaminant destruction for large fluxes of dilute contamination
- deployable at commercial scale within 2–3 years

The selected approach is the LLNL developed biofilter which meets all the criteria and is described in detail below.

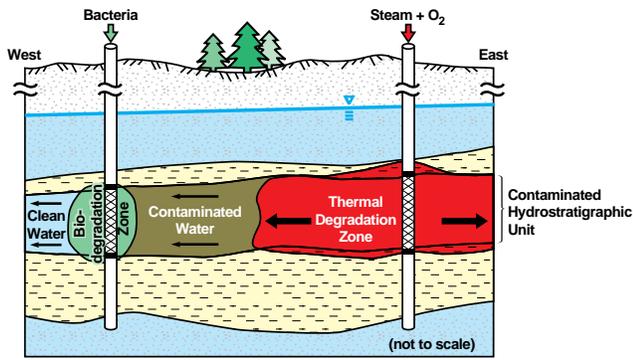


Figure 4: Illustration of the displacement of contaminated ground water caused by injection of large volumes of steam. To prevent dispersal of the contaminants in the source region, we propose to emplace in situ microbial filters which destroy contaminants as they pass through them.

A conceptual view of the complete strategy is given in Figure 5. The spatial extent of biofilter coverage necessary is a potentially important cost factor and will be determined in the demonstration experiments.

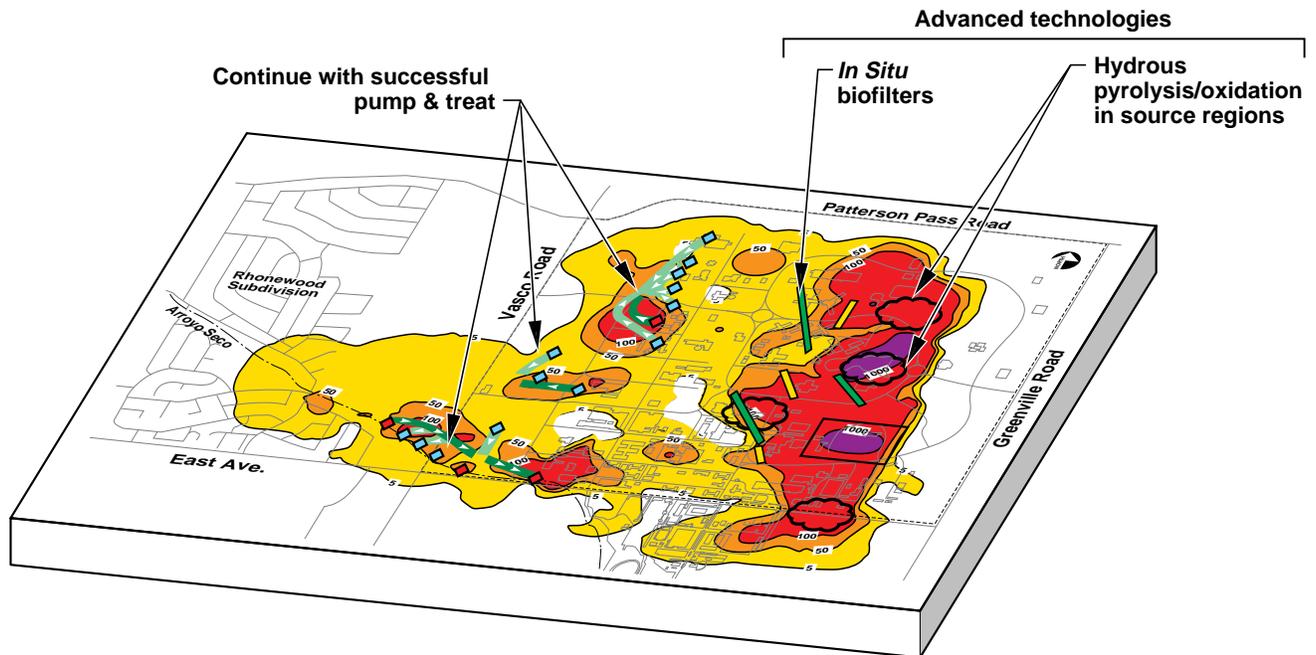


Figure 5. Schematic implementation of LLNL cleanup strategy using pump and treat, hydrous pyrolysis/oxidation, and biofilter.

The strategy described above depends on an accurate identification of the location of contaminants and the favored pathways for their migration. Using stratigraphic correlation methods from petroleum geology in concert with comprehensive characterization data from LLNL site investigations, we now understand the site well enough to accurately predict, for engineering purposes, where contaminants are located and where they are likely to be transported (Blake, 1996). This understanding allows contaminants in existing plumes to be tracked back to their high-concentration source areas. Consequently, instead of having to apply remediation methods to the entire site, source and distal areas can be targeted for treatment with the appropriate method.

### HYDROUS PYROLYSIS/OXIDATION

Hydrous pyrolysis/oxidation is an innovative process for the *in situ* destruction of solvents. The technique is expected to be applicable to both DNAPLs and dissolved organic components. These chemicals rapidly oxidize to carbon dioxide and chloride ion when heated to temperatures near the boiling point of water, provided sufficient dissolved oxygen or soil mineral oxidants are present. The method utilizes the established experience in heating large volumes of ground, developed in the Dynamic Underground Stripping Demonstration, to provide the delivery system for the heat and oxygen. Steam and oxygen are injected together, building a heated, oxygenated zone in the subsurface. When injection is halted, the steam condenses and contaminated ground water returns to the heated zone. It mixes with the condensate and oxygen, destroying any dissolved contaminants. This should avoid many of the mixing problems encountered in other *in situ* oxidation schemes. We expect that DNAPL will be destroyed in place, without surface treatment. This method takes advantage of the much more rapid chemical reactions which occur at steam temperature, as well as the large increase in mass transfer rates which make contaminants more available for destruction.

We are investigating the *in situ* thermal degradation of chlorinated hydrocarbons such as those found on the LLNL Livermore Site (TCE, PCE, DCE, etc.) as well as others such as PCB, pentachlorophenol, and refractory hydrocarbons (PAHs) via this method. Using the techniques of Dolfing and Janssen (1994), it can be shown that there is a significant thermodynamic driving force for the oxidation of these compounds at 25°C and one bar. This fact alone, of course, doesn't mean that the reaction will, in fact, proceed as written for a number of reasons. However, we have experimentally found that dissolved O<sub>2</sub> gas can rapidly and completely destroy TCE, producing benign products (predominantly CO<sub>2</sub> and Cl<sup>-</sup> anion), at

temperatures easily achieved by potential *in situ* thermal remediation techniques (Figure 6). At temperatures over approximately 90°C the TCE is completely removed to analytical detection limits in one to a few days, depending on the temperature. The TCE concentration in these particular tests with high starting concentrations decreased at least 10,000-fold. The products are those expected for complete oxidation to CO<sub>2</sub>.

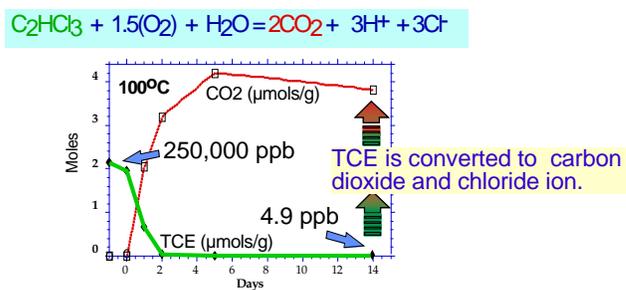


Figure 6. Laboratory results show that TCE can be rapidly destroyed at temperatures that are achievable by steam injection. Experiments were conducted in Dickson-type, gold-bag rocking autoclaves (Knauss et al., 1992; Knauss and Copenhagen, 1995a, 1995b; Jackson et al., 1992).

The tests at temperatures below approximately 90°C produced the same products, but the rates of TCE degradation were considerably slower. We are continuing to make oxidation rate measurements as a function of temperature in order to determine the activation energy of the reaction. Then we can calculate precisely the rate of TCE oxidation by O<sub>2</sub> gas at any temperature of interest.

We have also investigated the oxidation of TCE by mineral phases common in soils in the absence of excess dissolved O<sub>2</sub> gas at 100 and 150°C. The soil mineral MnO<sub>2</sub> can also oxidize TCE, again producing benign products (CO<sub>2</sub>, Cl<sup>-</sup> anion and Mn<sup>+2</sup> cation). However, at a given temperature the MnO<sub>2</sub> rate of TCE oxidation is much slower than oxidation via dissolved O<sub>2</sub> gas. This is at least partly due to the reaction being limited by the total surface area of the MnO<sub>2</sub>. In these initial experiments we used a very well crystallized mineral (pyrolusite) with very low specific surface area. Soil MnO<sub>2</sub> would be expected to be much more reactive. This would suggest that in a field application even those more distal areas, too far away to benefit directly from the injection of O<sub>2</sub> gas into a TCE "hotspot," would experience TCE degradation, because oxidants like MnO<sub>2</sub> are ubiquitous in soils. All that is needed is heat and time.

The potential for soil-mineral oxidation of TCE makes hydrous pyrolysis/oxidation potentially a very robust technique; there are a number of chemical reactions that will destroy TCE in soil, provided only that enough heat is supplied to make the reactions run at an acceptable rate.

A huff-and-puff treatment is planned as the prime treatment method.

1- Steam mixed with a small amount of oxygen is injected into a permeable zone to build a small steam zone.

2- Steam injection is halted, and ground water returns to the heated zone. About 1/15th of the water in the heated zone is condensed from the steam. Oxygen present in the steam dissolves in the water as the steam condenses.

3- Heat retained by the soil heats the returning ground water (and entrained TCE) to nearly 100°C. TCE is oxidized by the oxygen contained in the water.

4- Steam is reinjected, building a larger heated zone and repeating the oxidation process. The process is repeated until the steam zone growth is limited by heat loss to the edges.

The cyclic steaming ensures that any water displaced by the steam injection moves only a few meters before being pulled back through the hot zone and cleaned. Oxygen gas is used instead of air to increase the rate of oxidation while keeping injection temperatures high; the addition of inert gas reduces the partial pressure of steam in the system, and hence its boiling point. Direct replacement of oxygen by air would reduce the oxygen concentration by a factor of five, and hence the rate of oxidation would be reduced.

The time required to process TCE by this technique can be estimated from our existing data. If we make the assumption that the reaction rate order with respect to oxygen is one, then from our Arrhenius relationship we can calculate an approximate field of rates vs. temperature and oxygen content. At typical steam-zone-collapse pressures of 3–4 bar, approximately 100 ppm of oxygen is soluble in water (note that nitrogen is not present as in air, which enhances the oxygen solubility). Approximately 10 days would be required to destroy saturated TCE in water under these conditions. Note that the extrapolation to low temperatures indicates that the reaction would take 300 years under ambient conditions, confirming the field observation that oxidation of chlorinated solvents is not a significant ongoing natural process.

## IN SITU MICROBIAL FILTERS

In situ microbial filters employ a resting-state bioaugmentation technique to remediate contaminated ground water. In this method, naturally-occurring bacteria are grown in surface bioreactors, separated from their growth medium (resting-state), resuspended in an aqueous solution without the growth substrate, and then injected into the subsurface (bioaugmentation). The selected bacteria are nonpathogenic and pose no danger to human health. A significant fraction of the injected bacteria attaches to the aquifer media to create a fixed-bed in situ biofilter.

Fluid injection to establish an in situ biofilter occurs over a short period of time. After cell injection is terminated, the natural ground water flow regime reestablishes itself. However, this flow regime can be amplified by the upgradient steam injection in large quantities, or by nearby ground water extraction downgradient from the biofilter. Flowing ground water transports dissolved contaminants to the biofilter where they are biodegraded. The rate of biodegradation in the engineered biofilter is designed to balance the contaminant transport rate so that clean ground water exits the biofilter. Thus, the plume is prevented from further migration and is severed from its source region by this strategy. Further details can be found in Taylor, et al., 1993.

A recent field test at the Chico Municipal Airport demonstrated that an in situ biofilter using resting-state cells can effectively remediate ground water contaminated with chlorinated solvents. A pure strain methanotrophic bacteria was suspended in ground water and injected (at 4 L min<sup>-1</sup>) into an aquifer through a single well at a depth of about 28 m. The injected ground water was devoid of growth substrates and cosubstrates but did contain a tracer. Baseline studies at the injection location found the ground water to be contaminated with 425±50 ppb of TCE. Approximately 50% of the injected bacteria attached to the soil, forming an in situ, fixed-bed, quasi-spherical bioreactor with an average radius of about 1.2 m and an attached population density of approximately 500M cells per gram of aquifer material. Contaminated ground water was subsequently withdrawn through the biofilter by extracting water through the injection well at a rate of 4 to 2 L min<sup>-1</sup>. Results show that 98% of the TCE was biodegraded during the first 50 hours of ground water withdrawal (Figure 7). In the ensuing days, TCE concentrations at the withdrawal well gradually increased with biodegradation persisting until the experiment was terminated 40 days after initiation. This field test conclu-

sively demonstrated that an in situ biofilter can (1) successfully be emplaced into the subsurface, (2) decrease substantial contaminant concentrations to near regulatory limits, and (3) sustain degradation over extended periods of time. Further details can be found in Duba, et al, 1996.

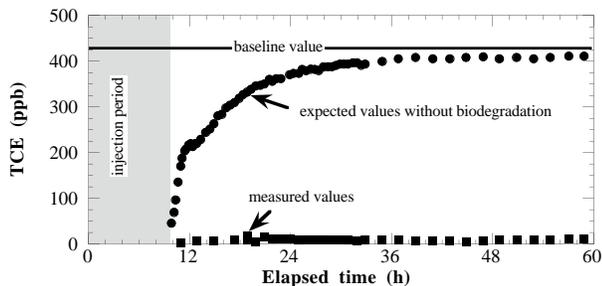


Figure 7. An emplaced biofilter reduced TCE concentrations by about 98% during the first 60 hours of operation. TCE concentrations expected without biodegradation were calculated from recovery of an injected tracer during the extraction phase.

The primary area of application at LLNL is the eastern part of the site where most of the contaminant sources are located. The main concept calls for emplacing in situ biofilters within the appropriate hydrostratigraphic units downgradient from contaminant sources and near the 100 to 50 ppb contaminant concentration contour interval. Natural ground water flow, augmented by steam injection upgradient from the biofilter and pump-and-treat extraction downgradient from the biofilter, will bring contaminants through the treatment zone where they will be degraded to harmless compounds such as aqueous  $\text{CO}_2$  and chloride ions before they exit.

## PROCESS MONITORING

Successful remediation is only partly dependent upon effective cleanup technology. Treatment technologies that will target contaminant sources as part of this initiative require an advanced level of monitoring for process control and performance assessment. Experience gained in monitoring other subsurface treatment tests will be used in process design and optimization for this project. In the Dynamic Underground Stripping Project, for example, the rapid response of the monitoring methods provided near-real time information about the thermal processes, thereby allowing engineers to effectively control the subsurface operations. Initial field applications in this project will be heavily instrumented to provide a detailed understanding of the subsurface processes as the overall operational strategy is optimized. With increased field experience, subsequent full-scale monitoring designs

will be streamlined, reflecting both the experience gained from the initial applications and the concurrent development of systems tailored to the project operational needs.

Cleanup methods are only as good as the ability to 1) place them where needed, 2) determine whether they are operating effectively, and 3) demonstrate regulatory compliance. Real-time process control systems will monitor steam injection, *in situ* oxygen levels, ground water flow, and *in situ* biofilter operation. Electrical Resistance Tomography (ERT), with its demonstrated ability to provide timely images of underground processes, will be a key tool for monitoring steam and biofilter operations. Fiber optic chemical sensors will be used in conjunction with the cleanup methods to monitor water chemistry for controlling oxygen- and microbe-injection processes. Tiltmeters will be used for large-area hydraulic control of steam injection and pumping processes.

Areas of the subsurface that are missed initially by thermal treatment will be identified through the ERT and tiltmeter measurements as well as sampling and analysis and targeted for further operations. This type of feedback was useful in gaining regulatory support for innovative cleanup processes during the Dynamic Underground Stripping project.

THE DEMONSTRATION PROJECT  
(ACCELERATED CLEANUP INITIATIVE)

A schematic representation of the main elements of the LLNL demonstration project called the Accelerated Cleanup Initiative (ACI) is given in Figure 8.

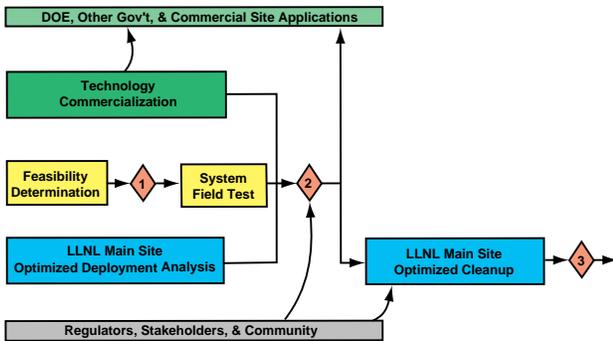


Figure 8. Overall structure of the Accelerated Cleanup Initiative.

Each of the activities, outcomes and decision points shown in Figure 8 are briefly described below.

*Feasibility Determination:* Demonstrate that the *in situ* conditions necessary for successful implementation of the proposed technologies at the LLNL Livermore Site are achievable.

*Decision Point 1:* Can we expect success in the field test at the LLNL Livermore Site?

*System Field Test:* Acquire information required to make the technical, financial, and regulatory decision to apply the proposed technologies at full scale.

*LLNL Livermore Site Optimized Deployment Analysis:* Produce optimized, accelerated LLNL site cleanup strategy using a combination of pump-and-treat and the proposed technologies.

*Technology Commercialization:* Train commercial firm(s) to implement proposed technologies by working in concert on the demonstration at LLNL.

*Decision Point 2:* Do the proposed accelerated cleanup technologies offer the best option at the LLNL Livermore Site and at other sites?

*DOE, Other Gov't. & Commercial Site Applications:* Develop the information necessary to meet the need for new approaches to significantly reduce the cost of contaminated ground water cleanup. This need is per-

ceived acutely by property owners who are prevented from selling or developing their property due to the lengthy duration of currently available cleanup methods, who have unacceptable remediation maintenance and operation costs, or who experience continuing negative community relations due to lack of closure. These include both private and government cleanups. Land use objectives, the relative value of current and future funds and the costs of the available remedies are all important factors which will be considered. Establishment of the costs of the proposed approach and guidelines for selection of the methods developed is an important outcome of this work.

*Regulators, Stakeholders, and Community:* Achieve informed consensus on accelerated cleanup and define an acceptable closure condition for the site.

*LLNL Livermore Site Optimized Cleanup:* Implement optimized, risk-based accelerated LLNL site cleanup strategy.

*Decision Point 3:* Do the appropriate regulatory agencies accept cessation of Livermore Site active remediation?

The first decision point is expected to occur at the beginning of FY97. With adequate funding the goal for reaching decision point 2 is the end of FY98.

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